PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

Applicants: BRUNNER ET AL-1

SERIAL NO.: 09/425,694 EXAMINER: M.SONG

FILED: OCTOBER 22, 1999 GROUP: 1765

TITLE: PROCESS FOR THE WET CHEMICAL TREATMENT OF SEMICONDUCTOR WAFERS

BRIEF ON APPEAL

ATTN: MAIL STOP AFTER FINAL AMENDMENT
Commissioner of Patents
P.O.BOX 1450
Alexandria, VA 22313-1450

Dear Sir:

This is in response to the Final Office Action dated November 14, 2002, and with a Notice of Appeal and Appeal Fee having been timely filed March 19, 2003, (with a Certificate of Mailing dated March 14, 2003).

A Petition for a four Month Extension of Time to file the Brief On Appeal is also enclosed herewith.

In accordance with the provisions of U.S.P.T.O. Rule 192 (c), paragraphs (1) to (9) are now presented.

(1) REAL PARTY IN INTEREST

The real party in interest, is the party named in the caption of the brief.

(2) RELATED APPEALS AND INTERFERENCES

There are no other appeals or interferences known to appellant, the appellant's legal representative, or assignee which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) STATUS OF CLAIMS

All of the pending claims are claims 1 to 9 and 11. Claim 10 has been canceled. The claims on appeal are claims 1 to 9 and 11.

(4) STATUS OF AMENDMENTS

All of the previously filed Amendments have been entered.

(5) SUMMARY OF INVENTION

The present invention relates to a process for the wet

chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, in particular a process for the cleaning of silicon semiconductor wafers. (Please see Page 1, first paragraph of the present Specification).

It is an object of the present invention to provide a process by which metallic impurities and particles can be removed particularly effectively from semiconductor wafers. (Please see Page 1, third paragraph of present Specification).

The above object is achieved according to the present invention by providing a process for the wet chemical treatment of semiconductor wafers, in which the semiconductor wafers are treated with treatment liquids, wherein the semiconductor wafers are firstly treated with an aqueous HF solution, then with an aqueous O_3 solution and finally with an aqueous HCl solution, these treatments forming a treatment sequence. (Please see paragraph bridging pages 1 and 2 of present Specification).

It has been found that the object is achieved by this treatment sequence, which does not need to be interrupted by rinsing with water or another treatment liquid and is carried out exclusively at a pH which is lower than pH 7. The treatment according to the invention with the treatment liquids indicated

is performed in treatment baths. It is preferable to circulate the treatment liquid, that is to take some of this liquid from the corresponding treatment bath and return it back after having been filtered. This saves on outlay for the required chemicals and for deionized water. The addition of fresh water or other liquids to the treatments baths is to be avoided since, when valves are opened, pressure impulses are created and particles can be introduced into the treatment baths. The treatment according to the invention is therefore different from a rinsing treatment, in which fresh treatment liquid is supplied continuously or at intervals. (Please see paragraph on Page 2 of the present Specification).

The present invention is characterized in that the wafers are treated with liquids in a specific sequence of baths, wherein an interruption of the treatment sequence by rinsing with water or another liquid must be strictly avoided.

As to the comparative examples disclosed in the present patent Specification, they clearly show the disadvantageous effect if the sequence is interrupted by a rinsing step with water even if megasonic waves are acting on the water during the rinsing step. Only the claimed combination of treatment steps with the final treatment with an aqueous HCl solution leads to an acceptable low number of particles on the wafers.

(6) ISSUES

The one issue presented in this Appeal is whether, or not, the final rejection of claims 1 to 11 under 35 U.S.C. 103 as being unpatentable over *Pirooz* in view of *Verhaverbeke*, should be affirmed, or should be reversed.

(7) GROUPING OF CLAIMS

All of the rejected claims stand or fall together.

(8) ARGUMENT

The final rejection of claims 1 to 11 (i.e. 1-9 and 11) is believed to be in error for the following reasons, and should be reversed.

The Patent Examiner has rejected claims 1 to 11 as being unpatentable under 35 U.S.C. 103 over *Pirooz EP 701,275* in view *Verhaverbeke U.S. Patent No. 6,132,522.* (It is respectfully submitted that *Pirooz* is not *EP0731498A2* which is *Fukuzawa).*

Neither, *Pirooz*, nor *Verhaverbeke*, teach or suggest the claimed three steps of firstly treating the semiconductor wafers

in a bath with an aqueous HF solution; only containing HF;

then treating the semiconductor wafers in a bath with an aqueous O_3 solution; only containing O_3,; and

then treating the semiconductor wafers in a bath with an aqueous HCl solution; only containing HCl;

whereby these treatment steps form a treatment sequence B_2,which avoids rinsing with water or another treatment liquid and the addition of fresh water or other liquids to the treatment baths.

In this Final Office Action, it is respectfully submitted that the Patent Examiner does not refer in a comprehensive way to the arguments that were presented in the Amendment filed August 14, 2002. For example, there is no comment on the differences between the claimed invention and *Verhaverbeke et al.*, especially that this reference does not disclose the step (i) of treating the wafers in a bath with an aqueous O_3 solution only containing O_3 and optionally HF and, after having performed (i), the step (ii) of treating the semiconductor wafers in a bath with an aqueous HCl solution only containing HCl and optionally O_3. Since the other reference cited by the Examiner, *Pirooz et al.*,also does not disclose (ii), it is immediately clear that even the

combination of both documents, which is not even suggested by the prior art, does not lead to the claimed invention.

Therefore, it is the Applicant's position that the present claims are clearly patentable over the cited prior art.

Moreover, the Office Action takes the position that a person having ordinary skill in the art would have found it obvious to modify *Pirooz's* procedure by treating the semiconductors wafers with O_3 and then treating the wafers with a liquid containing HCl in a separate bath in order to produce a more efficient procedure for removing metals from the surface. However, such a procedure is not in compliance with the teaching of *Verhaverbeke et al.* This teaching comprises directly displacing the volume of the first reactive process fluid by providing a second reactive process liquid (See. col. 16, lines 41-43).

If the Examiner's suggestion is true that a person having ordinary skill in the art would have found it obvious to modify *Pirooz* by eliminating the step of rinsing with water as taught by *Verhaverbeke et al.* in order to obtain good process performance, then consider the following. Why should this person at the same time adhere to the *Pirooz's* teaching of using separate treatment baths which probably impairs the process performance? Also

consider why should this person modify the *Pirooz's* process by treating the semiconductor wafers with O_3 and then treating the wafers with a liquid containing HCl in a separate bath which certainly impairs the process performance (because a single step is split into two separate steps).

In addition, why should a person having ordinary skill in the art have found it obvious to modify *Pirooz's* procedure by treating the semiconductor wafers with O_3 and then treating the wafers with a liquid containing HCl in a separate bath in order to produce a more efficient procedure for removing metals from the surface? This is because *Pirooz* actually teaches using ozone and HCl optionally, only (col. 3, lines 32-34). It would appear that the Patent Examiner has based these conclusions on the present invention teachings by using hindsight.

Therefore, a person skilled in the art would have no motivation at all to combine the references in the manner as suggested by the Patent Examiner.

In addition, *Pirooz* in columns 2 and 3 teaches the following:

substances which are optionally present only are enclosed into brackets.

Step A:

$HF:H_2O$ + [HCl] or HF: H_2O +- [H_2O_2] or HF: H_2O + [O_3]

Step B:

Rinsing with H_2O

Step C:

O_3 : H_2O +[HCl] or O_3 :H_2O + [HNO_3]

Step D:

Rinsing with H_2O

The reference *Verhaverbeke et al (US-6,132,522)* teaches, inter alia, a sequence of the following treatment agents (please see column 9, lines 34 - 42):

Step 1:	Step 1:
$HF:H_2O$	H_2O_2 : H_2O : NH_4 OH
Step 2:	Step 2:
H_2O_2 : H_2O : HCl or	H_2O_2 : H_2O : HCl
Step 3:	Step 3:
$H_2O_2:H_2O:NH_4OH$	$HF:H_2O$

In addition, according to *Verhaverbeke et al.* rinsing of the wafers between steps 1 to 3 is not required.

The present invention claims a procedure comprising a treatment with the following sequence of treatment agents:

Step i:

$HF:H_2O$ + [HCl] + [surfactant]

Step ii:

$O_3:H_2O$ + [HF]

Step iii:

HCl : H_2O + [O_3]

Also any rinsing step between steps i to iii is excluded.

Since the last mentioned feature is a crucial requirement of the present invention, *Verhaverbeke et al.* clearly qualifies to be considered as the closest prior art reference.

A comparison between *Verhaverbeke et al.* and the present invention reveals a significant difference between steps 2 and 3 (*Verhaverbeke*) and steps ii and iii (Invention) respectively.

Step 2 and step ii differ in that H_2O_2:H_2O: HCl (prior art) is used instead of O_3:H_2O (Invention) and step 3 and step iii differ in that H_2O_2:H_2O:NH_4OH(prior art) is used instead of HC1:H_2O.(Invention).

If the present invention is further compared with *Pirooz et al.*, two other differences can be found. *Pirooz et al.* teach in contrast to both the present invention and *Verhaverbeke et al.* a rinsing step with water (step B) and *Pirooz et al.* discloses a step C comprising a treatment with either O_3:H_2O+[HC1] or O_3:H_2O+[HNO_3], whereas according to the present invention two subsequent steps are necessary, i.e. step ii (a treatment with O_3:H_2O+[HF]) and then step iii (a treatment with HC1:H_2O + [O_3]).

Verhaverbeke is not combinable with *Pirooz* for the following reasons.

Verhaverbeke U.S. Patent No. 6,132,522 in column 3 in lines 9 to 22 discloses wet processing methods useful in the manufacture of electronic component precursors, such as semiconductor wafers and flat panels, used in integrated circuits. These methods can be used for the cleaning, stripping, and/or etching of such electronic component precursors.

It has been discovered that eliminating the DI rinse between each chemical treatment step minimizes precipitation of the silica, metal, and/or oxide precipitates. In contrast to the wet processing methodologies available in the art, which focus on rinsing the electronic component precursors with DI water between each chemical treatment step, the process eliminates the need for the DI rinse by using a sequential chemical methodology.

In column 9 in lines 7 to 28 *Verhaverbeke* discloses that in sequential chemical processes, the DI rinse between each chemical step is not required. In a sequential chemical process the vessel fills with DI water through valve 31, conditioning of temperature and flow take place, the first reactive chemical process fluid is injected into DI water stream flowing in 9 via injection lines (i.e., 17, 15). The first reactive chemical flows into the vessel through valve 31 into the vessel. The soak starts by closing valve 31. During the soak, conditioning of flow and temperature of DI water occurs through the DI bypass 45, by opening valve 47. Conditioning occurs only during the soak. At the end of the soak, the valves positions switch (i.e., valve 31 opens and 47 closes) and injection of the next reactive chemical process fluid occurs immediately through injection port 19 so that next reactive chemical process fluid directly displaces the previous reactive chemical process fluid (i.e., no DI water is used to displace chemical in the vessel). These steps

or similar steps known to persons skilled in the art may be repeated until the electronic component precursors are properly treated with the appropriate chemicals. Following the chemical treatment steps, the electronic component precursors may be dried as discussed above.

In column 10 in lines 15 to 45, *Verhaverbeke* discloses that the methods of this reference may be used where only one set of sequential chemical treatment occurs. For example, where the chemical treatment recipe is sulfuric acid (mixed with either peroxide or ozone)/HF/SCI/SC2, this is followed by drying. Traditionally, a DI water rinse is performed between each chemical treatment step. According to the methods of this reference, all of the DI water rinses may be eliminated or maybe only one or two rinses may be done between some, but not all, of the chemical treatment steps regardless of the wet processing technique employed.

As previously stated, traditional wet processing techniques use a DI water rinse between each chemical treatment step to prevent the chemicals from mixing with each other and to prevent contamination of one reactive chemical process fluid with another. *Verhaverbeke* departs from this principal, by not performing a DI water rinse between each chemical treatment step. However, in practicing the process of *Verhaverbeke*, it is

desirable to exchange the chemical solutions regularly to achieve reproducible processing. It is particularly preferred that the chemicals be exchanged after one use, while traditionally, chemicals are used for extended use. Adequate performance may be obtained with extended use by spiking (i.e., adding chemical to the second bath) to maintain a relatively constant concentration and pH. This, however, is still more efficient than the traditional techniques that use a DI water rinse between each chemical treatment step. A person skilled in the art would therefore never combine the teaching of *Verhaverbeke* (devoid of water rinsing) with *Pirooz* (employs water rinsing).

It is clearly non-obvious to replace a single step treatment taught by a prior art reference as a treatment which can be realized by choosing one of two possibilities by a two step treatment requiring the two possibilities in a specific order. Moreover, it still must be emphasized that *Pirooz et al.* teach intermediate rinsing with water which is contradictory to the teaching of *Verhaverbeke et al.* Hence any attempt to combine these references would constitute a radical reconstruction of the prior art which is impermissible according to 35 U.S.C. 103.

Accordingly, both references absolutely cannot be combined so as to disclose the claimed invention.

In the Advisory Action dated March 5, 2003, the Patent Examiner contended as follows.

This is in response to Applicant's argument that the Examiner does not refer in a comprehensive way to the arguments presented in the Amendment filed August 14, 2002. The Patent Examiner stated that no comment between the presently claimed invention and *Verhaverbeke et al* was made because the *Verhaverbeke* reference is a secondary reference used to show the obviousness of using a process without a DI water-rinsing step. A proper Graham vs. Deere analysis of the primary reference, *Pirooz et al*, was made to show the differences between the prior art and the instantly claimed invention.

In response to Applicant's argument that modifying a procedure of *Pirooz et al* by treating the semiconductor wafers with O_3 and then treating the wafers with a liquid containing HCl in a separate bath is not in compliance with the teaching of *Verhaverbeke et al* is noted but has not been found persuasive. The Applicant's argument is based on a teaching in *Verhaverbeke et al* that comprises directly displacing the volume of the first reactive fluid by providing a second reactive process liquid (column 16, lines 41-43). This is only one specific embodiment of *Verhaverbeke et al* and the reference is not as limited as

suggested by Applicant. *Verhaverbeke et al* also teaches another embodiment where the electronic component is moved from one reaction chamber to another, wherein each reaction chamber contains a different reactive chemical process fluid (column 3, lines 55-60).

In response to Applicant's argument that the Examiner's conclusion of obviousness is based upon improper hindsight reasoning, it must be recognized that any judgment on obviousness is in a sense necessarily a reconstruction based upon hindsight reasoning. But so long as it takes into account only knowledge which was within the level of ordinary skill at the time the claimed invention was made, and does not include knowledge gleaned only from the Applicant's disclosure, such a reconstruction is proper.

In response to Applicant's argument that a comparison between *Verhaverbeke et al* and the present invention reveals significant differences is noted but has not been found persuasive. Firstly, the *Verhaverbeke et al* reference is used as a secondary reference to modify the primary reference, *Pirooz et al*. The Applicant has incorrectly attempted to show *Verhaverbeke et al* to be the closest prior art. Furthermore, Applicant's arguments against the references individually, cannot show non-

obviousness by attacking references individually where the rejections are based on combinations of references. The differences between the instant invention and the *Verhaverbeke et al* reference are allegedly taught by *Pirooz et al*.

In response to Applicant's argument that a person skilled in the art would never combine the teaching of *Verhaverbeke et al* with *Pirooz* has been noted but has not been found persuasive. This is a mere allegation without any factual support, and therefore is not given consideration. Furthermore, the *Pirooz* reference teaches a chemical treatment step using DI water and the *Verhaverbeke et al* reference teaches a method of improving a chemical treatment by eliminating a DI water-rinsing step (column 3, lines 15-20).

The Applicants answer these contentions of the Patent Examiner as follows.

If the Examiner's opinion is accepted that it would have been obvious to modify *Pirooz et al* by eliminating the DI water-rinsing step as taught in the *Verhaverbeke et al* reference in order <u>to improve the chemical treatment</u> (process efficiency) then the Examiner should have also explained the following. Why would it be obvious to modify in addition the teaching of *Pirooz et al*

with regard of the treatment step with ozonated water in a manner which obviously impairs the process efficiency again? According to *Pirooz*, the metals removal is carried out in an aqueous solution containing HF, water and optionally HCl and ozone. This means doubtlessly that according to *Pirooz* a single process step is sufficient.

However, according to the claimed invention, two different process steps are mandatory, namely first treating the wafers in one bath with aqueous ozone and optionally HF and subsequently in another bath with aqueous HCl and optionally ozone. However, if the Examiner's motivation for combining *Pirooz* and *Verhaverbeke et al* is still the same, i.e. an improvement in the process efficiency, then it cannot be concluded in a persuasive way that someone who is skilled in the art would have omitted the DI water-rinsing on the one hand in order to improve the efficiency, and on the other hand would have split the single step taught by *Pirooz* in a two step procedure. This clearly diminishes the process efficiency again, and therefore would counteract the motivation to combine these references as stated by the Patent Examiner.

The teaching of *Verhaverbeke et al* that electronic component precursors are moved from one reaction chamber to another,

wherein each reaction chamber contains a different reactive chemical process fluid, does not matter at all in this context. This is because *Verhaverbeke et al* neither teaches a step of first treating the wafers in one bath with aqueous ozone and optionally HF nor subsequently treating the wafers in another bath with aqueous HCl and optionally ozone.

Further evidence of the non-obviousness and of the patentability of the claimed invention can be seen from the attached analysis of features ("Merkmalsanalyse"). This is a comparison between the features of the independent claims of the present application and the disclosure of the closest prior art references which were cited by the Patent Examiner.

If a claim feature is found in the respective reference, it is marked with a plus sign (+). Otherwise a minus sign (-) indicates that the respective feature is missing.

As previously referred to in the Brief on Appeal, the *Pirooz* reference discloses a sequence of steps A to D, only steps A and C being steps which comprise a treatment with an aqueous solution containing a chemical substance. However, the treatment sequence which is claimed in the present invention mandatorily requires at least three different treatment steps with an aqueous solution containing a chemical substance.

In addition, there is no proper argument that the *Pirooz* disclosure would suggest such a third treatment step.

Since the second reference, namely *Verhaverbeke et al.*, does not disclose the claimed treatment sequence, it is not possible to suggest the claimed invention by any combination of the cited references. This is also revealed by the attached analysis.

CONCLUSIONS

In view of all the reasons set forth above, all the claims must be considered as being non-obvious under 35 U.S.C. 103 with respect to the prior art applied by the Patent Examiner. Reversal of this ground of rejection is respectfully requested.

Respectfully submitted,

BRUNNER ET AL-1, (CPA)

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Enclosures: 1) Appendix (9)
2) Comparative Analysis (2 pgs)

I hereby certify that this correspondence is being deposited with the U.S. Postal Service as first class mail in an envelope addressed to: Commissioner of Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on September 12, 2003.

_____
Marie Guastella

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(9) APPENDIX

In this appendix is a copy of the claims involved in this appeal:

1. A process for the wet chemical treatment of semiconductor wafers with treatment liquids in baths, comprising the steps of

firstly treating the semiconductor wafers in a bath with an aqueous HF solution only containing HF and optionally HCl and optionally a surfactant;

then treating the semiconductor wafers in a bath with an aqueous O_3 solution only containing O_3 and optionally HF; and

then treating the semiconductor wafers in a bath with an aqueous HCl solution only containing HCl and optionally O_3;

whereby these treatment steps form a treatment sequence B_2, which avoids rinsing with water or another treatment liquid and the addition of fresh water or other liquids to the treatment baths.

2. The process as claimed in claim 1,

wherein the treatment sequence B_2 is preceded by a treatment B_1 of the semiconductor wafers with an aqueous SC-1 solution.

3. The process as claimed in claim 1,

wherein the treatment sequence B_2 is followed by a treatment B_3 comprising drying the semiconductor wafers.

4. The process as claimed in claim 3,

wherein the treatment of the semiconductor wafers is sequenced according to the term $m^* (B_1 + B_2) + B_3$,

m being an integer number and the treatment B_1 and the treatment sequence B_2 being carried out in succession, and

this taking place m times, before the drying treatment B_3 is performed.

5. The process as claimed claim 1,

wherein in treatment sequence B_2, the aqueous HF solution contains HF in a concentration of from 0.001% to 2% by weight and optionally HCl in a concentration of up to 2% by weight and optionally a surfactant; and

wherein all percents by weight are based upon the total solution weight.

6. The process as claimed in claim 1,

wherein in treatment sequence B_2, the aqueous O_3 solution contains O_3 in a concentration of from 1 ppm to 30 ppm and is optionally exposed to megasonic waves.

7. The process as claimed in claim 1,

wherein the treatment liquid used last in the treatment sequence B_2 contains ozone and is optionally exposed to megasonic waves.

8. The process as claimed in claim 3,

wherein the drying treatment is carried out using a step selected from the group consisting of centrifuging, using hot water, using isopropanol, and using marangoni principle.

9. The process as claimed in claim 2,

wherein in treatment B_1 the aqueous SC-1 solution contains a liquid selected from the group consisting of NH_4OH and H_2O_2, and TMAH (= tetramethylammonium hydroxide) and H_2O_2.

11. A process for the wet chemical treatment of semiconductor wafers with treatment liquids in baths, comprising the steps of

firstly treating the semiconductor wafers in a bath with an aqueous HF solution only containing HF and optionally HCl and optionally a surfactant;

then treating the semiconductor wafers in a bath with an aqueous O_3 solution only containing O_3 and optionally HF; and

then treating the semiconductor wafers in a bath with an aqueous HCl solution only containing HCl and optionally O_3 with exposure to megasonic waves,

whereby these treatment steps form a treatment sequence B_2, which avoids rinsing with water or another treatment liquid and the addition of fresh water or other liquids to the treatment baths.

Merkmalsanalyse ST9822 US (application 09/425,694)

assignee: **WSAG**
filing date: **22.10.99**
priority: **19.11.1998**

claim 1	EP701275 (Pirooz)	US6132522 (Verhaverbeke et al.)
A process for the wet chemical treatment of semiconductor wafers with treatment liquids in baths, comprising the steps of	+	+
firstly treating the semiconductor wafers in a bath with an aqueous HF solution only containing HF and optionally HCl and optionally a surfactant;	+	+
then treating the semiconductor wafers in a bath with an aqueous O_3 solution only containing O_3 and optionally HF; and	+	-
then treating the semiconductor wafers in a bath with an aqueous HCl solution only containing HCl and optionally O_3;	-	-
wereby these treatment steps form a treatment sequence B_2, which avoids rinsing with water or another treatment liquid and the addition of fresh water or other liquids to the treatment baths.	-	+

claim 11	EP701275 (Pirooz)	US6132522 (Verhaverbeke et al.)
A process for the wet chemical treatment of semiconductor wafers with treatment liquids in baths, comprising the steps of	+	+
firstly treating the semiconductor wafers in a bath with an aqueous HF solution only containing HF and optionally HCl and optionally a surfactant;	+	+
then treating the semiconductor wafers in a bath with an aqueous O_3 solution only containing O_3 and optionally HF; and	+	-
then treating the semiconductor wafers in a bath with an aqueous HCl solution only containing HCl and optionally O_3 with exposure to megasonic waves;	-	-
wereby these treatment steps form a treatment sequence B_2, which avoids rinsing with water or another treatment liquid and the addition of fresh water or other liquids to the treatment baths.	-	+